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Slurry sampling for determination of lead in marine plankton by electrothermal atomic absorption spectrometry

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Abstract

A slurry sampling method has been developed for the determination of Pb in marine plankton by ETAAS using a freshwater plankton certified reference material (CRM 414). Slurries were prepared in 1–3% m/v range with 1% v/v HNO₃ by ultrasonic agitation for 5 min. The effects of several chemical modifiers, including Ir(NO₃)₂, Mg(NO₃)₂, Pd(NO₃)₂, Pd(NO₃)₂ + Mg(NO₃)₂, and Mg(NO₃)₂ + NH₄H₂PO₄, were investigated for the stabilization of Pb during thermal pretreatment. Lead in slurries was effectively stabilized up to 1000 °C with Ir, Pd and Pd+Mg modifiers among which Pd+Mg provided the best results with complete atomization at 1850 °C. Firings in the presence of Ir were, problematic due to ash formation inside the atomizer. Water, dilute HNO₃ and HF were examined as suspension medium. Dilute HNO₃ (1–2% v/v) proved to be advantageous over water as it afforded extraction of Pb from plankton almost quantitatively in 5 min agitation. Hydrofluoric acid was the least suitable medium. Increasing HF concentration up to 5% v/v resulted in inaccuracy and substantial background absorption. Fast-heating furnace method provided comparable accuracy and precision to that of conventional-heating in slurries of CRM 414. Detection limits and characteristic masses were, respectively, 0.49 µg L⁻¹ and 32 pg for the conventional method and 0.62 µg L⁻¹ and 37 pg for the fast-heating method. However, fast-heating approach suffered from distorted peaks at high temperatures and incomplete pyrolysis of matrix at lower temperatures. Analysis of marine plankton samples for Pb was performed by using the conventional furnace program. The results showed a high correlation with those obtained by solution ICP-MS. Differences were statistically insignificant within 95% confidence interval.

Keywords: Slurry sampling, Lead, Plankton, ETAAS

1. Introduction

Slurry sampling has become an attractive approach since its first introduction in 1974 by Brady et al. [1] for determination of trace elements by electrothermal atomic absorption spectroscopy (ETAAS) [2–6]. The most frequently cited advantages of slurry sampling include rapid sample preparation without using corrosive or concentrated acids, reduced risks of contamination and loss of volatile elements since the preparation is often performed at room temperature. Another unique advantage of slurry sampling over solid sampling is the compatibility with aqueous standardization, which consequently makes slurry sampling highly preferable approach for rapid, quantitative determinations at trace levels [1–6].

Contrary to wet sampling, the accuracy and precision in slurry sampling suffer from the issues of particle size, homogeneity and slurry concentration. In comparison to nebulization systems (e.g., FAAS and ICP), ETAAS is more tolerant to particle size effects due to absence of a nebulizer and relatively longer residence time of particles in the atomizer [6,7]. Nevertheless, incomplete atomization and poor precision occur for slurries with particle size larger than 50 µm, which have been attributed to poor sampling and slower vaporization of larger particles from the graphite furnace platform [2,6–8]. Conversely, several studies reported successful determinations with particles as large as 300 µm [9–11]. It was pointed out that the uniformity of the particle size was more influential on the precision, which was better for coarse particles (e.g., 250–600 µm) than for particles smaller than 250 µm [9].

Slurries are usually prepared by suspending finely ground powder of sample in water [12,13] or dilute nitric acid [5,11,14];

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the latter is preferred as it aids in the extraction of trace elements into solution. Hydrofluoric acid (HF) has been also used as a suspension medium for refractory and siliceous samples [15–19]. Depending on analyte concentration and sample type, the concentration of slurries varies between 0.5 to 5% m/v. Precision degrades with highly diluted and concentrated slurries due to the variations in sampling and delivery of representative aliquots onto the furnace. For stabilization of slurries, a number of viscous reagents, such as Triton X-100 [9,13,14], glycerol [20,21] and hexametaphosphate [22] have been used, while homogeneity is usually achieved by means ultrasonic agitation [4,9,10,14], magnetic stirring [12,13,15] and vortex mixing [23,24]. Among these procedures, ultrasonic agitation has been highly popular as it improves the extraction of the analyte of interest into the liquid phase, especially when slurries are prepared in acidic medium [2–6].

In slurry sampling ETAAS, fast-heating and conventional-heating approaches have been alternatively used for the atomization of samples [25,26]. In the former, the pyrolysis step is omitted and the drying is performed at a relatively high temperature. This approach has been applied to the analysis of siliceous samples [12,15–19], coal and fly ash [14] and biological samples [24,27]. The precision and accuracy were reported to be comparable to those obtained by conventional-heating approach [14,19,25], in which high temperature ashing is performed to destroy volatile matrix components in the presence of chemical modifiers. Thus far, a number of chemical modifiers have been proposed for the stabilization of Pb during thermal pretreatment, including $\text{Ir}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$ in plant and sediment materials [4], $\text{Pd}(\text{NO}_3)_2$ in particulate matter [5], $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$ in sediments [13,28], and human hair [21], $\text{NH}_4\text{H}_2\text{PO}_4$ in food samples [29], and $\text{NH}_4\text{H}_2\text{PO}_4 + \text{Mg}(\text{NO}_3)_2$ in plant and animal tissues [30]. Hydrofluoric acid [16,17,19,31–33] and polytetrafluoroethylene (PTFE) [34,35] have also been used as chemical modifier in a different sense to eliminate the matrix in the analysis of slurries of siliceous samples. The effect of HF and PTFE were attributed to their fluorinating action to convert silicates to volatile silicon tetrafluoride.

In an attempt to determine uptake limits of heavy metals in marine phytoplankton, we have developed a slurry sampling method using freshwater plankton material for the determination of Pb by ETAAS. The efficacy of nitric acid and hydrofluoric acid as suspension medium were evaluated for the extraction of Pb from plankton as well as for the elimination of the matrix interferences. The effects of a number of chemical modifiers were examined on the stabilization and atomization of Pb in plankton

slurries. The performances of fast-heating and conventional-heating approaches were also evaluated in terms of precision and accuracy of the results. The method was validated through the analyses of freshwater plankton certified material and then applied to the quantification of Pb in marine plankton samples.

2. Experimental

2.1. Reagents and standard solutions

All reagents were of analytical grade. High-purity deionized distilled water with a resistivity of $18 \text{ M}\Omega \text{ cm}^{-1}$ was used to prepare standard solutions and slurries. Calibration standards were prepared from a $10 \mu\text{g mL}^{-1}$ Pb standard solution that was prepared from $1000 \mu\text{g mL}^{-1}$ stock Pb standard solution (Fisher Scientific). Nitric acid (Fisher Scientific) was purified by sub-boiling. Hydrofluoric acid (EM Science) solution was ultra-pure (99.995%). Aqueous solutions of $\text{Pd}(\text{NO}_3)_2$ (Perkin-Elmer), $\text{Mg}(\text{NO}_3)_2$ (Fisher Scientific), $\text{NH}_4\text{H}_2\text{PO}_4$ (BDH) and $\text{Ir}(\text{NO}_3)_2$ (Perkin-Elmer) were used as chemical modifiers, which contained 10 mg mL^{-1} Pd^{2+} , Mg^{2+} , PO_4^{3-} and Ir^{2+} , respectively. All glassware and containers were cleaned in 5% v/v HNO_3 bath and rinsed with water before use.

2.2. Instrumentation and data collection

A Perkin-Elmer (Norwalk, CT, USA) Model 4100ZL atomic absorption spectrometer equipped with a longitudinal Zeeman background correction system, a transversely heated graphite atomizer (THGA) and an AS-71 autosampler was used. Pyrolytically coated graphite tubes from Perkin-Elmer (Part No B0504033) containing an integral L'vov platform were used throughout. Standard and sample aliquots ($30 \mu\text{L}$) were delivered by AS-71 autosampler. Lead hollow cathode lamp (Perkin-Elmer) operating at 10 mA was used as the light source. The 283.3-nm line and 0.7 nm spectral width were used. Argon was used as purge gas. The default value (90%) of the magnetic field strength was used corresponding to a magnetic field strength of 0.84 T. A 50-watt ultrasonic processor unit (Sonics & Material Inc., Danbury, CT, USA) equipped with a 2-mm diameter titanium probe was used. The ultrasonic unit was operated as recommended by the manufacturer. The operating parameters of the conventional-heating and the fast-heating furnace programs are summarized in Table 1. The instrument was interfaced to a personal computer which controlled the spectrometer and the THGA furnace, and processed the data

Table 1
Operational settings of THGA for conventional- and fast-heating furnace programs

	Conventional-heating					Fast-heating		
	Dry 1	Dry 2	Ashing	Atomization	Clean	Dry	Atomization	Clean
T ($^{\circ}\text{C}$)	150	400	950	1850	2400	500	1850	2400
Ramp (s)	5	10	5	0	1	10	0	1
Hold (s)	10	25	30	5	2	20	5	2
Ar (mL min^{-1})	250	250	250	0	250	250	0	250
Read				Yes			Yes	

using GEM based software (version 3.1). Integrated absorbances were measured for triplicate firings of standards and slurries.

2.3. Marine plankton samples

Freeze-dried plankton samples (3H) were provided by the NOAA/National Marine Fisheries Service (NMFS) Laboratory, Milford, CT. The particular plankton cultures were grown in simulated seawater under the following controlled concentrations of trace metal nutrients: Sr 30 mg L⁻¹, Al 10 mg L⁻¹, As, Cd, Pb, Hg, Sn, Tl and Eu 0.5 mg L⁻¹. The predicted elemental concentrations, assuming all the elements to be consumed during the growth, would be Sr 150 µg g⁻¹, Al 50 µg g⁻¹, As, Cd, Pb, Hg, Sn, Tl and Eu 2.5 µg g⁻¹ on dry basis.

A second batch of plankton samples (3H-Se) were grown with identical trace element concentrations, but enriched with different concentrations of selenium (Se) as an additional nutrient element to investigate the effect of Se on planktonic growth and trace metal accumulation of profile. The concentrations of Se added to the growth medium were as follows: 130 mg L⁻¹ for 3/27/97 plankton sample, 13 mg L⁻¹ for 5/1/97 and 5/8/97 plankton samples, and 1.3 mg L⁻¹ for 6/5/97 and 6/12/97 plankton samples.

2.4. Method development and optimization

The optimization of the conditions for pyrolysis temperature, chemical modifiers and atomization temperature were carried out by univariate method with slurries of freshwater plankton (CRM 414). To test the efficacy of chemical modifiers, six slurries (~1% m/v) were prepared with 1.0 mL deionized water in 2-mL polyethylene vials. No modifier was added to the first vial, while others contained one of the following of the chemical modifiers: 17 µL of Ir(NO₃)₂, 17 µL Pd(NO₃)₂, 17 µL Mg(NO₃)₂, 17 µL Pd(NO₃)₂+17 µL Mg(NO₃)₂ or 17 µL Mg(NO₃)₂+170 µL NH₄H₂PO₄. The slurries were homogenized for 2–3 min by ultrasonic probe. The temperature of THGA was varied from 500 to 1200 °C. Triplicate firings were made for slurries at 2000 °C by injection 30 µL volumes onto the platform. In each injection, slurries contained either 0, 5 µg Ir, 5 µg Pd, 5 µg Mg, 5 µg Pd+5 µg Mg or 5 µg Mg+50 µg PO₄ as chemical modifier premixed with the sample.

The mass of each element in 30-µL injection volume was further optimized between 1 and 15 µg for the best modifier (e.g., Pd+Mg), for which pyrolysis and atomization profiles for a slurry were reexamined with those of a 40 µg L⁻¹ Pb solution to identify the optimum furnace conditions. First, pyrolysis temperature was varied between 700 and 1300 °C. Later, atomization temperature was studied from 1500 to 2000 °C at the optimum pyrolysis condition.

The effects of water, dilute HNO₃ and HF as suspension media were investigated on the accuracy and precision. The concentrations of the acids in the slurries were varied from 1 to 5% v/v. The period of ultrasonic agitation was varied from 5 to 20 min in 5 min increments to affect the extraction of Pb from plankton slurries (~1% m/v). At the end of each period, triplicate firings were made for 30 µL slurries. Immediately

after, the slurries were centrifuged and firings were made from aqueous phase. The effect of slurry concentration on the precision and accuracy was examined between 0.2 and 3% m/v that were prepared in 1% v/v HNO₃. Possible contamination to Pb from the titanium probe was tested with blank solutions containing 0 to 5% v/v HNO₃ for 15 min sonication.

In the last stage of method development studies, a fast-heating furnace program was developed without using any chemical modifier to evaluate its suitability for determination of Pb in plankton by slurry sampling ETAAS. The atomization temperature was kept constant at 1850 °C as for the conventional-heating program (see Table 1). The drying temperature was varied from 400 to 600 °C to investigate the effects of fast-heating on background, peak shape, accuracy and precision. Slurries were made in 1% m/v HNO₃.

2.5. Method validation and calibration

A fresh water plankton reference material (CRM 414, Trace Elements in Plankton) purchased from BCR (Brussels, Belgium) was used for method validation. Five replicate analyses were made by using the conventional- and fast-heating furnace programs (Table 1). External calibration was performed with aqueous Pb standard solutions prepared in 10-mL calibrated flasks with 1% v/v HNO₃. The external standards were 0, 1, 2, 5, 10, 20, 40 and 60 µg L⁻¹ that all contained 100 µL of 5 mg mL⁻¹ Pd(NO₃)₂+Mg(NO₃)₂ modifier. For determinations by fast-heating furnace program, a second set of standard solutions within the same range were prepared without adding any modifier. Triplicate firings were made for each solution by injecting 30 µL volumes. The mean integrated absorbances for 0–20 µg L⁻¹ were used to calculate the Pb concentration in marine plankton (3H), while all standards were included in the calibration curve for the freshwater plankton. Calibration plots were linear within the concentration range (0–60 µg L⁻¹); correlation coefficients (r) ranged from 0.996 to 1.00.

2.6. Procedures

The particle size of CRM 414 was reported to be less than 125 µm [36].³¹ The slurries were prepared in 1% m/v range without any further grinding. The sample was homogenized for 2–3 min by shaking the bottle prior to sampling. Approximately 10–13 mg samples were directly weighed into the 2-mL volume autosampler vials. To the vials, 20 µL of 5 mg mL⁻¹ Pd(NO₃)₂+Mg(NO₃)₂ modifier solution was added and the volume was completed 1 mL with 1% v/v HNO₃ (980 µL). The contents were homogenized by sonicating for 5 min at 40-watt power. Injections (30 µL) onto the L'vov platform were made while agitating the slurries.

For marine plankton slurries, freeze-dried samples were ground using an agate ball mill, and then sieved through 212 µm apertures. Slurries were prepared within 3% m/v range by placing approximately 30–35 mg of sieved samples into the autosampler vials. All other treatments were performed as for the CRM samples. Mass correction for the water content was also made for the plankton samples by drying approximately

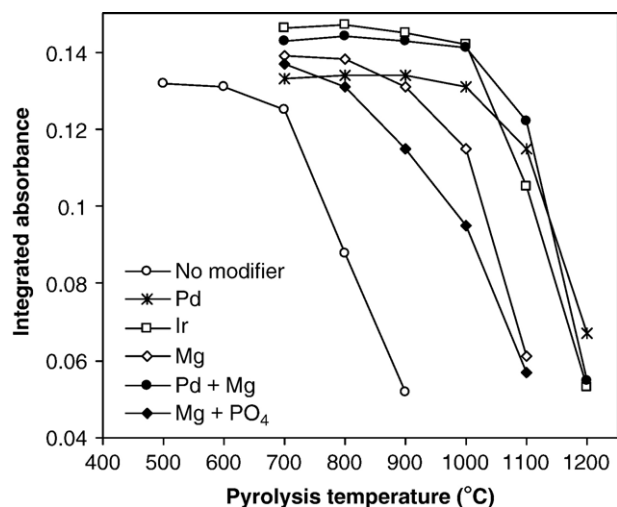


Fig. 1. The effect of modifiers on stabilization of Pb in fresh water plankton slurries ($\sim 1\%$ m/v) in water. Modifiers are added into the slurry and homogenized by ultrasonic probe for 5 min. Injection volume is $30\ \mu\text{L}$. The mass of each element is $5\ \mu\text{g}$ and $50\ \mu\text{g}\ \text{PO}_4$ per injection [$T_{\text{atom}}=2000\ ^\circ\text{C}$].

100 mg masses of the materials in an oven at $100\ ^\circ\text{C}$ for 1–2 h. The water compositions were 3.5 and 3.3% m/m for freshwater plankton and marine plankton, respectively.

3. Results and discussion

3.1. Chemical modifiers and pyrolysis conditions

The pyrolysis curves for Pb obtained with different chemical modifiers from the slurries of freshwater plankton are illustrated in Fig. 1. Lead was unstable above $700\ ^\circ\text{C}$ when slurries did not contain any modifier. Maximum pyrolysis temperature was about $1000\ ^\circ\text{C}$ which was achieved with Ir, Pd and Pd+Mg modifiers. Lead was stable up to $800\ ^\circ\text{C}$ in the presence of Mg and $\text{Mg}+\text{NH}_4\text{H}_2\text{PO}_4$, but this temperature was neither

comparable to those obtained with Ir, Pd and Pd+Mg modifiers, nor was sufficiently high to destroy the organic matrix of plankton.

Despite its effectiveness, the firings with $5\ \mu\text{g}$ Ir were problematic. An ash developed on the platform after 5–6 firings which resulted in distorted peaks. It was necessary to remove the ash mechanically as it could not be removed by successive empty firings. Such problem did not occur with Pd modifier, nor did with Pd+Mg. Both modifiers appeared equally suitable for high temperature stabilization of Pb to effectively destroy the volatile matrix components. However, the integrated absorbance obtained in the presence of Pd+Mg was consistently higher (ca. 0.01 A) when compared to that with Pd alone (see Fig. 1); therefore, Pd+Mg mixed modifier was used throughout and the pyrolysis temperature was set to $950\ ^\circ\text{C}$. Further examination of Pd+Mg composition indicated that $3\ \mu\text{g}$ Pd+ $3\ \mu\text{g}$ Mg was sufficient to achieve comparable results to that of $5\ \mu\text{g}$ Pd+ $5\ \mu\text{g}$ Mg without any loss of Pb at $950\ ^\circ\text{C}$.

3.2. Atomization conditions

In ETAAS, atomization temperature impacts the performance of analysis substantially. High atomization temperatures are detrimental to graphite tube that in due course add to the background absorption considerably due to the atomization of carbonaceous material from the graphite atomizer, whereas at lower temperatures precision and accuracy deteriorate if the analyte of interest is not fully atomized [4]. The latter is a common issue in slurry sampling because of the interference of the sample matrix, especially with large particles, to alter the efficiency of the chemical modifier and subsequently that of atomization between samples and aqueous standards [6,21,25]. The effects of such interferences on the absorbance profiles (peak height, appearance time etc) can easily be alleviated by using integrated absorbance measurements provided that a sufficiently high atomization temperature is chosen to ensure high precision between replicate firings [6–8].

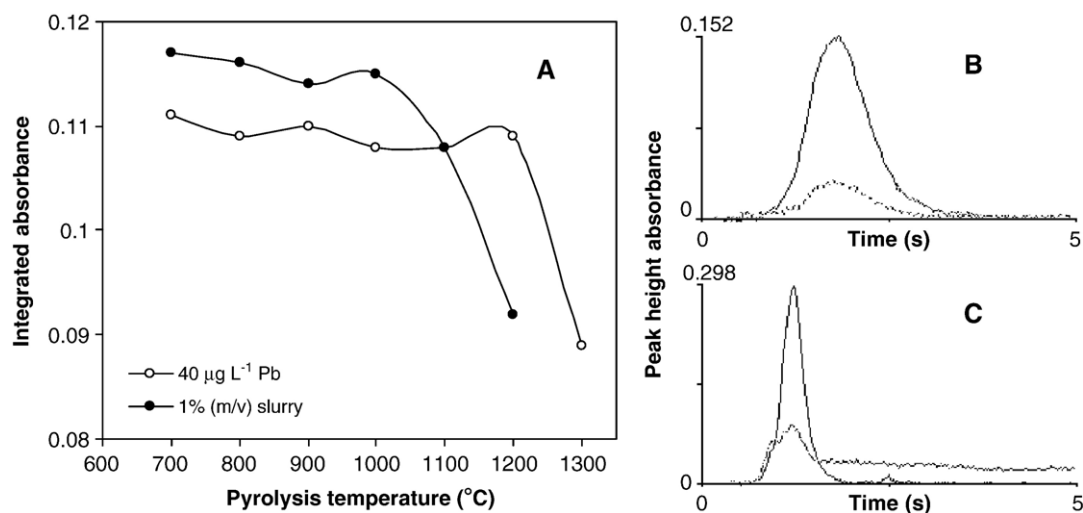


Fig. 2. The effect of $3\ \mu\text{g}$ Pd+ $3\ \mu\text{g}$ Mg modifier on stabilization and atomization profiles of Pb. Pyrolysis curves for slurries and $40\ \mu\text{g}\ \text{L}^{-1}$ Pb standard solution (A); atomization profile from $40\ \mu\text{g}\ \text{L}^{-1}$ Pb standard solution (B); atomization profile from 1% m/v plankton slurry (C). [$T_{\text{atom}}=1850\ ^\circ\text{C}$].

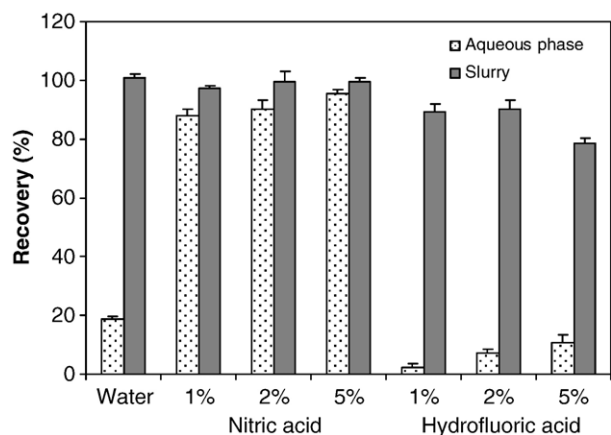


Fig. 3. The effect of suspension medium on the recovery (e.g., accuracy) and relative extraction of Pb from freshwater plankton slurries (~1% m/v). Each slurry was agitated ultrasonically for 5 min and 30 μ L containing 3 μ g Pd+3 μ g Mg modifier were dispensed onto the platform. [$T_{\text{pyrolysis}}=950$ °C; $T_{\text{atom}}=1850$ °C].

In freshwater plankton slurries, Pb was fully atomized within 3–4 s at around 1500 °C. However, this temperature was not high enough for firings of aqueous standard (40 μ g L⁻¹) for which Pb absorption was manifested by a broad and noisy peak which did not reach the baseline in 5 s. The pyrolysis curves given in Fig. 2A suggest that this behavior was the consequence of the over-stabilization of Pb (e.g., up to 1200 °C) in standard solution by the modifier (3 μ g Pd+3 μ g Mg). Such over-stabilization was also observed for Pb in different samples [21,37,38]. Complete atomization from the standard solutions occurred at 1850 °C. For triplicate firings of 40 μ g L⁻¹ Pb solution, precision (RSD) ranged between 0.5 and 4% indicating the residual atomization was insignificant. The resulting absorption profiles of Pb were similar to those in Fig. 2B and C for standards and slurries, respectively. The peaks from the slurries were sharp and narrow (short-lived) in comparison to those from the standards, which was mainly because of the reduced stability of Pb in slurry as well as the rapid sweep of the analyte from light path by the rapidly expanding background gases in the atomizer. This pattern, however, did not have any significant effect on the accuracy

since integrated absorbance is virtually free from these interferences provided that analyte is not lost during pyrolysis.

3.3. Effect of extraction medium

In slurry sampling, the suspension medium not only aids in the extraction of analyte to aqueous phase to improve precision and accuracy, but also acts as a chemical modifier to get rid of the matrix constituents. In this sense, dilute HNO₃ has been frequently used in the preparation of slurries of biological and siliceous materials [4,7,27,29,30]. The addition of dilute HF to slurries was recommended for soil and sediments to eliminate silicon as volatile SiF₄ prior to atomization [15,16,31,32].

Plankton are mainly composed of organic material, and to some extent contain silicon which is an essential element for planktonic growth [39,40]. Thus, we investigated the performance of dilute HF as a suspension medium for plankton slurries in addition to water and dilute HNO₃. The results are illustrated in Fig. 3. In terms extraction of Pb from plankton, dilute HNO₃ provided the best results; relative extraction efficiency was about 88, 90, and 96% for 1, 2 and 5% v/v HNO₃, respectively, when slurries were submitted to ultrasounds for 5 min. The fraction of Pb in aqueous phase was about 19% for water, and 2, 7 and 11% for slurries prepared in 1, 2, and 5% v/v HF, respectively. Agitation up to 20 min did not provide any significant improvement in the results, suggesting that 5 min sonication was sufficient to effectively extract Pb from plankton by dilute HNO₃ for which recoveries from the atomization of slurries ranged between 97 and 100% (Fig. 3); relative standard deviation (RSD) for triplicate firings was always better than 5%.

Hydrofluoric is more aggressive on dissolution of silicates than organic matrix. While the poor results for HF extracts might be indicative of low Pb levels in the silicate skeleton of the plankton, the major drawback of HF as a suspension medium was on the accuracy that decreased from 101% (water or no HF) to 78% for slurries containing 5% v/v HF. This was probably because of the loss of Pb as relatively volatile PbF₄ (mp≈600 °C) during thermal pretreatment. Moreover, HF displayed no benefit in decreasing the background signals (Fig. 4) unlike those reported with soil and sediments [15–19]. The background absorption tended to increase with increasing

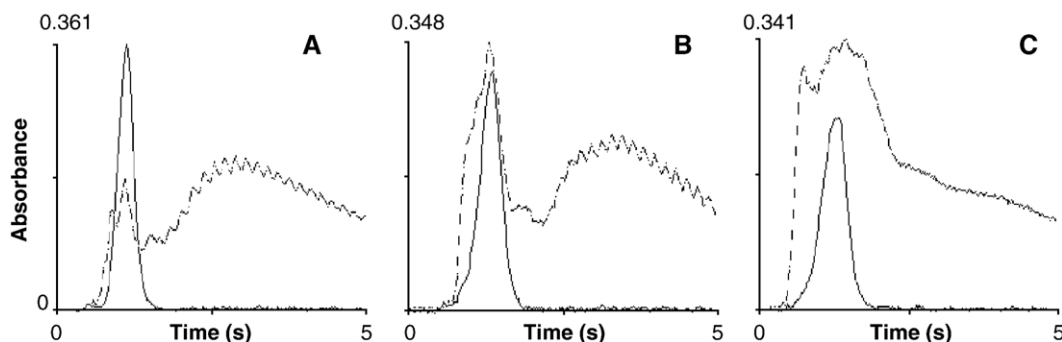


Fig. 4. The effect of HF on absorption of Pb (solid line) and background (dashed line). Approximately 1% m/v slurries of freshwater plankton in 1% v/v HF (A); 2% v/v HF (B); 5% v/v HF (C). [$T_{\text{pyrolysis}}=950$ °C; $T_{\text{atom}}=1850$ °C].

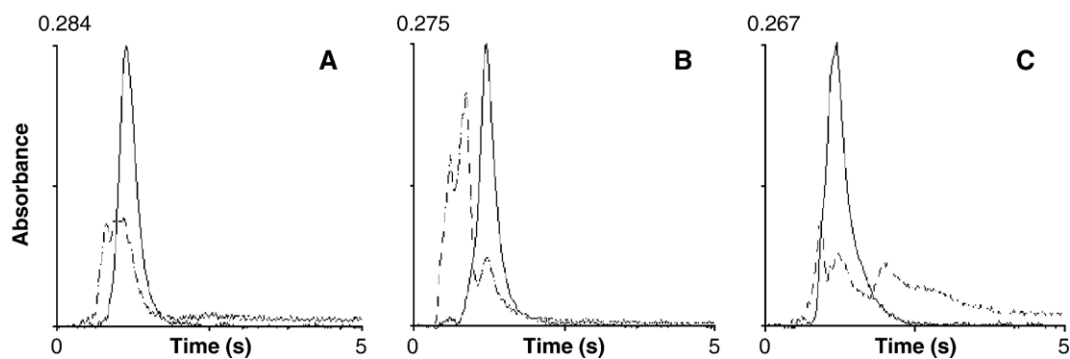


Fig. 5. Absorbance profiles for Pb (solid line) and background (dashed line) obtained from atomization of freshwater plankton slurries using conventional-heating program in the presence of 3 μg Pd+3 μg Mg modifier (A); fast-heating furnace program $T_{\text{drying}}=400$ °C (B); fast-heating furnace program $T_{\text{drying}}=500$ °C (C). Slurries were made in 1% m/v HNO_3 , $T_{\text{atom}}=1850$ °C.

HF concentration in the plankton slurries such that for 5% v/v HF the analyte signal was underneath that of the background (Fig. 4C). Such behavior was not observed with water, nor with dilute HNO_3 , did suggest that presence of HF inhibit the oxidation of organic material. Another problem associated with HF was the deterioration of the titanium probe of the ultrasonic processor. Especially for slurries in 5% v/v HF, agitations for 10 min caused a visible thinning of the titanium probe and consequently ruptured the tip immersed in solution in the following operations. On the other hand, deterioration of the probe in 5% v/v HNO_3 was very slow and was insignificant when slurries were made with 1 or 2% v/v HNO_3 . Possible contamination to Pb from the degradation of probe was verified by measuring blank absorbance for 5% v/v HNO_3 sonicated up to about 15 min. The blank signals varied between 0 and 0.003 A s that were also insignificant to confound the determinations from the plankton samples.

3.4. Slurry concentration

The experiments performed with slurries made in 1% v/v HNO_3 indicated that the minimum concentration of slurry was about 0.5% m/v for which accuracy ranged between 95 and 99% with RSD of about 5% for triplicate firings. Working with diluted slurries (e.g., 0.2% m/v) resulted in poor accuracies as low as 68% and relatively higher RSD (8–10%). Concentrated slurries (1 to 3% m/v) afforded better precision (RSD=0.5–2%) without any significant degradation in sampling and dispensing efficiency. In the analysis of freshwater plankton for method validation, the slurry concentration was not modified and kept constant at 1% m/v since the concentration of Pb was relatively high. For marine plankton samples, ICP-MS analysis [40] revealed that content of Pb was at least an order magnitude lower than in freshwater plankton; therefore, slurries were made in 3% m/v range to achieve accurate determination.

3.5. Effect of fast-heating approach

The main purpose of fast-heating approach in ETAAS is to increase sample throughput by reducing the analysis time as well

as to extend the lifetime of the graphite atomizer. Practically, high temperature pyrolysis step used in conventional-heating approach is replaced by a relatively short, low temperature drying stage without affecting the stability of analyte in the atomizer. In the conventional-heating furnace program, the maximum drying temperature for Pb without any chemical modifier was about 700 °C (Fig. 1). Thus, we investigated three different drying temperatures, 400, 500 and 600 °C, for developing a fast-heating program. A 5-s ramp was used to increase the furnace temperature to the desired value. For either temperature setting, it took approximately 20 s for the slurry (30 μL) to reach dryness (monitored through and adjustable mirror). The sample was dried for an additional 10 s and then atomized at 1850 °C. Typical absorbance profiles for Pb and background are shown in Fig. 5 along with that obtained by conventional-heating program. A large background absorption was observed for drying at 400 °C due to the incomplete ashing of organic matrix (Fig. 5B). This problem was overcome when the drying was performed at 500 °C, however, the Pb absorption peak was slightly distorted (Fig. 5C). This pattern probably originated from a visually invisible sputtering from slurries, because there was a “sizzling” sound from the sample within the first 15–20 s of the drying stage. At 600 °C, substantial sputtering occurred when the furnace was heated up to the temperature in 5 s, which caused contamination and blocking on the quartz windows. Subsequent atomization of the sample

Table 2

The results (mean \pm 95% confidence level) for Pb obtained from freshwater plankton (CRM 414) by slurry sampling using conventional- and fast-heating ETAAS

Replicate	Fast program		Conventional program	
	Found ($\mu\text{g g}^{-1}$)	Accuracy (%)	Found ($\mu\text{g g}^{-1}$)	Accuracy (%)
1	4.10	103	3.91	98.6
2	3.88	97.7	4.00	101
3	3.76	94.8	3.82	96.4
4	4.08	103	4.07	103
5	4.02	101	3.87	97.6
Mean	3.96 \pm 0.19		3.93 \pm 0.13	

Certified value is 3.97 \pm 0.19 $\mu\text{g g}^{-1}$ (mean \pm 95% confidence level).

resulted in the formation of shoulders and double peaks. These results are supported by those of Hinds et al. [12] who also observed distorted peak shapes and double peaks for drying temperatures above 400 °C in the determination of Pb from soils by fast-heating ETAAS.

3.6. Method validation and figures of merits

On the basis of these results, we opted for 500 °C for the fast-heating program with a modified temperature ramp of 10 s to avoid sputtering, and then applied to the determination of Pb from freshwater plankton (CRM 414). Slurries (~1% m/v, $n=5$) were prepared in 1% v/v HNO₃ by submitting to ultrasounds for 5 min. They were first analyzed by the fast-heating program followed by the conventional-heating program after adding necessary volumes of Pd(NO₃)₂ and Mg(NO₃)₂ modifiers to each slurry and agitating briefly. The results are summarized in Table 2. Paired *t*-test did not show any significant differences between the results of the two approaches at 95% confidence level; $p=0.60 > p=0.05$, $df=4$, $n=5$). Nor were the results statistically significantly different than the certified value at 95% confidence level; *t*-test, $p=0.98 > p=0.05$ for conventional-heating program and $p=0.47 > p=0.05$ for fast-heating program. In terms of detection capability, both approaches were equally suitable. The detection limits (3 s, $n=11$) and the characteristic masses for Pb were 0.49 µg L⁻¹ and 32 pg for the conventional program and 0.62 µg L⁻¹ and 37 pg for the fast program.

3.7. Determination of Pb in marine plankton

The marine plankton (3H) samples had been analyzed by inductively coupled plasma mass spectrometry (ICP-MS) for trace element content for which results were discussed elsewhere [40]. Briefly, the 3H plankton samples were digested in concentrated HNO₃/HF using microwave-assisted digestion. Semi-quantitative ICP-MS analysis revealed that the samples contained substantial levels of sodium (~150–250 mg g⁻¹).

Table 3
The results obtained from marine plankton slurries (~3% m/v) by conventional furnace program ETAAS and by ICP-MS after closed vessel microwave-assisted digestion with HNO₃/HF

3H Plankton	Harvest date (M/D/Y)	Pb concentration (µg g ⁻¹)	
		ETAAS ^a	ICP-MS ^b
1	3/27/97	0.091±0.008	0.079
2	5/1/97	0.265±0.023	0.261
3	6/5/97	0.255±0.034	0.270
4	6/19/97	0.074±0.01	0.064
5	6/26/97	0.446±0.018	0.537
6	3/27/97-Se	0.208±0.012	0.200
7	5/1/97-Se	0.247±0.025	0.265
8	5/8/97-Se	0.223±0.01	0.235
9	6/5/97-Se	0.186±0.014	0.188
10	6/12/97-Se	0.302±0.012	0.353

Growth medium for samples 6 through 10 were enriched with selenium.

^a Results are given as mean±standard deviation for 3 replicate measurements.

^b Results are given as mean of ²⁰⁸Pb and ²⁰⁷Pb values for 1 replicate measurement (Ref. [40]).

Because these samples were grown in simulated seawater, high concentration of sodium was indicative of presence of chloride at similar levels which may induce high background and even volatilization interferences without any chemical modifier resulting in the loss of Pb as PbCl and PbCl₂ (mp=501 °C) in ETAAS [41]. Thus, the analysis by ETAAS was performed using the conventional-heating protocol in the presence of 3 µg Pd+3 µg Mg modifier in the slurried samples (~3% m/v). The results are given in Table 3 along with those obtained by ICP-MS analysis. Relative standard deviation was slightly higher (7–8%) for triplicate firings of the slurries, mainly because of the lower concentration of Pb in 3H plankton compared to that in freshwater plankton. Nonetheless, there was a high correlation between the results of slurry sampling ETAAS and ICP-MS ($r=0.983$). Paired *t*-test did not detect any significant differences at 95% confidence level ($p=0.16 > p=0.05$, $df=9$). Comparison of the means for the 3H and 3H-Se (selenium enriched samples) did not yield any significant differences either ($p=0.93 > p=0.05$, $df=4$, $n=5$), indicating that presence of selenium as a nutrient in the growth medium had no significant influence on the accumulation of Pb by marine plankton.

4. Conclusions

Slurry sampling proves to be a powerful tool for accurate determination of Pb in freshwater and marine plankton by ETAAS. Both water and nitric acid are suitable for rapid preparation of slurries of plankton samples without going through aggressive acid digestion procedures. Nitric acid as a suspension medium is more advantageous over water as it promotes efficient extraction of Pb via ultrasonic agitation and oxidation of organic material during thermal pretreatment. It is concluded that hydrofluoric acid is not suitable at all for slurry preparation because of the volatilization interferences, prevailing background absorption and detrimental effects to the titanium probe. Despite the fact that Ir(NO₃)₂ has afforded high temperature stabilization of Pb, the modifier has interestingly precluded the pyrolysis of organic matrix of plankton, even at 1000 °C. The ash built-up inside the atomizer has reduced both precision and accuracy, and hence, the utility of this modifier for analysis of plankton by slurry sampling ETAAS.

Under the optimum conditions, fast-heating ETAAS has provided comparable performance for Pb as for the conventional furnace approach for freshwater plankton (CRM 414). Peak distortion, loss of analyte via sputtering, and incomplete pyrolysis of matrix components are, however, the major issues that require careful optimization of the furnace operating parameters. In this regard, increasing HNO₃ concentration (e.g., 5% v/v) and pyrolysis for a longer time may improve the removal of organics. In the case of marine plankton, presence of sodium chloride is expected to reduce the stability of Pb in the atomizer at temperatures (e.g., 500 °C) used to alleviate the background absorption from freshwater plankton. These temperatures do, however, have the risks for the loss of Pb as relatively volatile PbCl or PbCl₂; therefore, the use of fast-heating approach is not recommended, but the conventional-heating program with Pd+Mg(NO₃)₂ modifier.

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